

PATENT SPECIFICATION

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(54) ALKENYL SUCCINIMIDES

(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, E.C.2, a company incorporated in accordance with the Laws of England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

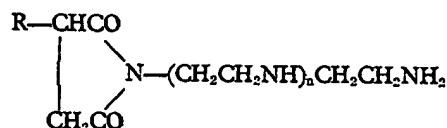
10 This invention relates to ashless detergent/dispersant additives for lubricating oils.

In the lubrication of some diesel engines running on high sulphur content fuel having an upper cylinder lubrication system e.g. marine diesels, it is necessary to use an upper cylinder lubricant having a highly basic nature i.e. having a high total base number. These lubricants usually contain an overbased metal salt such as an overbased calcium or barium phenate or sulphonate. However metal-containing salts are ash forming i.e. when they are burnt there is a metal-containing residue. It would be desirable to use an ashless basic additive for such applications.

25 Known ashless dispersant/detergent additives are the long chain alkenyl substituted succinimides, the alkenyl chain is usually derived from a polyalkylene e.g. a polyisobutylene. However these additives do not have a very high total base number. If an alkenyl moiety having a shorter chain is used as the alkenyl substituent then the succinimide is not oil-soluble and cannot be used in lubricating oils.

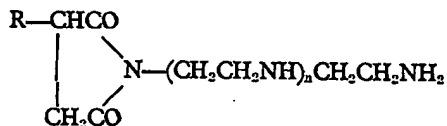
35 We have now discovered an oil soluble alkenyl succinimide having a high total base number.

40 According to the invention there is provided an N-amino-alkenyl succinimide of general formula

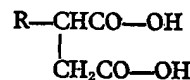


where R is a C_{2-20} alkenyl group and n is 0 to 10, preferably 1 to 5. Preferably R is a C_{4-15} alkenyl group.

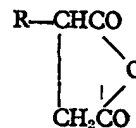
The invention also provides a method of preparing compounds of general formula:—



where R and n are as defined above, which comprises reacting an alkenyl substituted succinic acid or anhydride of formula:—



or



with a mixture of a polyamine of formula $\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH})_n\text{CH}_2\text{CH}_2\text{NH}_2$ where R and n are as defined above, and a primary mono-amine.

The primary mono-amine is preferably a C_{1-20} branched or straight chain aliphatic

[Price 25p]

amine more preferably a C_{4-16} amine.

The primary mono-amine is not present in the final product, it reacts with the acid or anhydride but is recovered from the reaction mixture. Without the presence of the primary mono-amine a mixture of cyclic and polymeric oil insoluble products are obtained of varying molecular weight.

The reaction preferably takes place in an inert solvent such as an aromatic hydrocarbon e.g. benzene, toluene or a xylene; the higher boiling solvents are the more preferable. The water formed during the reaction can be readily removed by distillation e.g. by refluxing the reaction mixture and for this the boiling point of any inert solvent and the primary mono-amine should be higher than that of water. The reaction preferably takes place at a temperature above the boiling point of water, 100°C.

After the reaction unreacted primary mono-amine can be removed by vacuum distillation.

Preferably excess primary mono-amine should be used and the polyamine and succinic acid or anhydride are preferably used in a substantially equi-molar proportion.

Some polymeric materials are also formed in a small amount of this reaction, and these are usually oil insoluble. These can be separated from the N-amino-alkenyl succinimide formed by extraction of the N-amino-alkenyl succinimide with an alkane e.g. n-heptane.

Preferably the compounds of the present invention have a total base number of at least 100 and more preferably 150. Compounds with a total base number of 200 or higher may also be formed by the process of the present invention. The total base number may be determined by test method ASTM 0664-58.

Generally speaking the more amine groups in the polyamine the higher the total base number.

The reaction of an alkenyl substituted succinic acid or anhydride with a polyamine in the absence of a primary mono-amine results in the formation of cyclic products which are oil insoluble and do not have a high total base number. It is very surprising that the presence of a primary mono-amine can result in the formation of a N-amino-alkenyl succinimide.

The invention will now be described with reference to the following Examples.

Example 1

55 9.55 grms (0.05 molar) of a mixture of branched chain primary amines of general formula $C_{12}H_{22}NH_2$ sold under the Trade

Name Primene 8IR was mixed with 5.45 grm (0.05 molar) of diethylene triamine and the mixture was added to a solution of 13.3 grm (0.05 molar) solution of dodecenyl succinic anhydride in toluene (200 ccs) and the solution refluxed for 1 hour through a "Dean and Stark" column till no more water was removed. The solution was evaporated to remove the solvent and then distilled under reduced pressure to recover the primary mono-amine. The residual oil was filtered.

Example 2

The procedure of Example 1 was repeated except that tetra-ethylene tetramine was used in place of diethylene triamine, and after filtration the residual oil was extracted with n-heptane to leave behind a polymeric insoluble residue. The n-heptane was then evaporated to give the desired product.

Example 3

Example 2 was repeated using tetra-ethylene pentamine in place of tri-ethylene tetramine.

Example 4

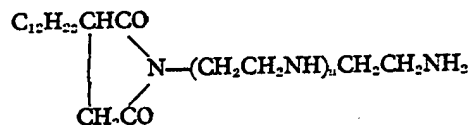
6.5 grms (0.05 molar) of n-octylamine was mixed with 5.45 grm (0.05 molar) diethylene-triamine and the mixture had added to it a solution of 13.3 grm (0.05 molar) of dodecenyl succinic anhydride in xylene (200 ccs) at below 30°C, and the solution was refluxed for 1 hour through a "Dean and Stark" column till no more water was removed. The solution was evaporated to remove the solvent and then distilled under reduced pressure to recover the primary mono-amine. The residual oil was filtered.

Example 5

Example 4 was repeated using a mixture of 1.5 grm (0.025 molar) of ethylene diamine and 2.72 grm (0.025 molar) of diethylene triamine instead of the diethylene triamine.

The structure of the products of Example 1-5 was determined by IR and NMR and the total base number determined.

The compounds had the general formula



and their total base numbers are shown below in the table 1.

TABLE 1

Example	n	Total Base Number (mg KOH/grm)
1	1	190
2	2	200
3	3	250
4	1	200
5*	$\frac{1}{2}$	170

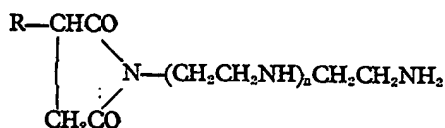
*n = $\frac{1}{2}$ is an average value

All the products were oil soluble.

- 5 The products of Examples 4 and 5 dissolved in about 30% concentration in a lubricating oil which was a blend of a solvent refined oil of viscosity index of 73 and viscosity at 110°F of 110.6 centistokes and a solvent refined oil of viscosity index of 95 and a viscosity of 21.35 centistokes at 100°F.
- 10 The blends were tested in the Ruston Engine Test for any signs of wear and were compared with a commercially available anti-wear additive. It was found that the additives caused no more wear than the anti-wear additive.
- 15 Thus the products of the invention are alkaline non-ash forming oil-soluble alkenyl substituted succinimides.

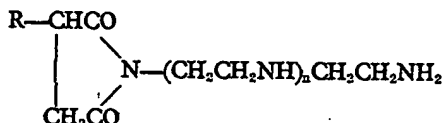
WHAT WE CLAIM IS:—

- 20 1. N-amino-alkenyl succinimides of general formula

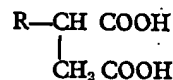


where R is a C₂₋₂₀ alkenyl group, and n is 0 to 10.

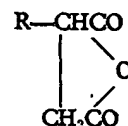
- 25 2. Compounds as claimed in claim 2 in which n is 1 to 5.
3. Compounds as claimed in any one of claims 1-3 in which R is a C₄₋₁₅ alkenyl group.
- 30 4. A method of preparing an N-amino-alkenyl succinimide of general formula



where R is a C₂₋₂₀ alkenyl group and n is 0 to 10 which comprises reacting an alkenyl substituted succinic acid or anhydride of formula



or



where R is as defined with a polyamine of formula



group where n is 0 to 10.

5. A method as claimed in claim 6 in which n is 1 to 5.

6. A method as claimed in any one of claims 3-5 in which R is a C₄₋₁₅ alkenyl group.

7. A method as claimed in any one of claims 3-6 in which the primary amine is a C₁₋₂₀ straight or branched chain aliphatic amine.

8. A method as claimed in claim 9 in which the primary amine is a C₄₋₁₅ aliphatic amine.

9. A method as claimed in any one of claims 3-8 in which the reaction takes place in an inert solvent.

10. A method as claimed in claim 11 in which the solvent is benzene, toluene or xylene.

11. A method as claimed in any one of claims 3-10 in which the primary amine is in excess.

12. A method as claimed in any one of claims 3—11 in which the polyamine and the succinic acid or anhydride are reacted in substantially equimolar quantities.
- 5 13. A method as claimed in any one of claims 3—12 in which the reaction is carried out at above 100°C.
14. A method as claimed in claim 3 as hereinbefore described with reference to the
- 10 Examples.
15. N-amino-alkenyl succinimides when prepared by the method of any one of claims 3—13.
- 15 16. Compounds as claimed in any one of claims 1—3 or 15 which have a total base number of at least 100.
17. Compounds as claimed in claim 15 which have a total base number of at least 150.
18. A lubricating composition comprising a lubricating oil and an N-amino-alkenyl succinimide as claimed in any one of claims 1—3, 15, 16 or 17.
- 20 19. A composition as claimed in claim 18 in which the N-amino-alkenyl-succinimide is 25 present in an amount of 1—15% by weight.

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